

11. (Twice Amended) The method for manufacturing a semiconductor device according to claim 1, said method further comprising;

a step, performed before said CVD high melting point metal nitride film forming step, of heating a substrate onto which said dielectric film is formed, in said chamber [by] while introducing therein said non-reactive gas; and

a step of forming said high melting point metal nitride film on said dielectric film by introducing a gas mixture comprising said  $\text{NH}_3$  gas and said non-reactive gas, said non-reactive gas in an amount equal to or larger than said  $\text{NH}_3$  gas, and said source gas containing said high melting point metal in an amount less than said  $\text{NH}_3$  gas and said non-reactive gas.

#### REMARKS

This paper is being provided in response to the April 5, 2001 Final Office Action for the above-referenced application. In this response, applicant has amended claims 1 and 11 in order to more particularly point out and distinctly claim that which Applicant deems to be the invention. Applicant respectfully submits that the amendments to the claims are all supported by the originally filed application.

The rejection of claims 1-29 under 35 U.S.C. §103(a) as being obvious over Nishikawa et al. (U.S. Patent No. 6,087,261, hereinafter referred to as "Nishikawa") in view of Tamaru et al (U.S. Patent No. 6,103,566, hereinafter referred to as "Tamaru") and further in view of Lee et al. (U.S. Patent No. 6,010,940, hereinafter referred to as "Lee") is hereby traversed and reconsideration thereof is respectfully requested. Applicant respectfully submits that the claims, as amended herein, are patentable over the

cited references, whether taken separately or in any combination. Applicant notes that claim 12 was cancelled in the previous response dated January 24, 2001.

Claim 1, as amended herein, recites a method for forming a semiconductor device having a laminated structure of a dielectric film made from a metal oxide which is formed on a surface of a substrate and a CVD high melting point metal nitride film directly formed on the metal oxide. The metal nitride film is directly formed on the dielectric film by introducing a source gas containing the high melting point metal into a chamber in which the substrate is contained. The method has a step of treating the substrate in an ambient that is non-reactive with respect to the metal oxide film formed on the substrate in the chamber where the non-reactive ambient includes a gas non-reactive with respect to the metal oxide and/or  $\text{NH}_3$  gas. The method recites keeping the temperature of the substrate at a prescribed temperature, before the source gas containing the high melting point metal is introduced into the chamber.

Claims 2 through 7 depend from claim 1 and recite further patentable features over the base claim. Dependent claim 2 recites that the treating step has a flow stabilizing step. Dependent claim 3 recites that the non-reactive gas is introduced during the flow stabilizing step. Dependent claim 4 recites that the treating step heats the substrate and the flow stabilizing step is after the heating step. Dependent claim 5 recites that the  $\text{NH}_3$  gas is introduced into the chamber during the heating step. Dependent claim 6 recites that the  $\text{NH}_3$  gas has a  $\text{NH}_3$  partial pressure of no greater than 1.0 Torr and no less than 0.1 Torr. Dependent claim 7 recites that the non-reactive gas and the  $\text{NH}_3$  gas are introduced into the chamber during the flow stabilizing step.

Claim 8 recites a method for forming a semiconductor device having a laminated structure of a dielectric made from a metal oxide and a CVD high melting point metal nitride film formed. The metal nitride film is directly formed on the dielectric film by introducing a source gas containing the high melting point metal into a chamber in which the substrate is contained. The method heats a substrate to a prescribed temperature in an  $\text{NH}_3$  atmosphere of no greater partial pressure than 1.0 Torr and no less than 0.1 Torr before the introduction of the source gas containing the high melting point metal.

Claims 9-10 depend from claim 8 and recite further patentable features over the base claim. Dependent claim 9 recites a step of heating the substrate to a prescribed temperature and maintaining the temperature in a non-reactive gas with respect to the metal oxide and while the gas flow is stabilized. Dependent claim 10 recites that the  $\text{NH}_3$  gas is introduced during the substrate heating step or the flow stabilization step.

Claims 11 and 13-29 depend from claim 1 and recite further patentable features over the base claim. Dependent claim 11, as amended herein, recites a step that is performed before the CVD high melting point metal nitride film is formed, of heating the substrate (on which the dielectric film is formed) in the chamber while introducing the non-reactive gas. Then performing a step of forming the high melting point metal nitride film on the dielectric film by introducing a gas mixture comprising the  $\text{NH}_3$  gas and the non-reactive gas, the non-reactive gas being in an amount that is larger than the  $\text{NH}_3$  gas, and the source gas amount being less than the  $\text{NH}_3$  and non-reactive gas. Dependent claim 13 recites that the dielectric film is a tantalum oxide ( $\text{Ta}_2\text{O}_5$ ) film. Dependent claim

14 recites that the substrate is heated to between approximately 400°C and 700°C.

Dependent claim 15 recites that the non-reactive gas is selected from a list of nitrogen, argon, hydrogen gas, or a mixture of these gases. Dependent claim 16 recites that the high melting point metal nitride film is a TiN film. Dependent claim 17 recites that the source gas containing titanium is selected from the group consisting of titanium tetrachloride (TiCl<sub>4</sub>), tetrakis dimethyl amino titanium (TDMAT), tetrakis diethyl amino titanium (TDEAT). Dependent claim 18 recites that the high melting point metal nitride film is alternately a WN film, and WF<sub>6</sub> gas is introduced as a source gas. Dependent claim 19 recites that the device has a capacitive element, a dielectric film, a CVD high melting point metal nitride film as a protective film between the dielectric film and the capacitive element. Dependent claim 20 recites that the device has a MOSFET where the CVD high melting point metal nitride layer is the lowermost layer of the laminated gate electrode layer. Dependent claim 21 recites raising the partial pressure of the NH<sub>3</sub> gas during a second half of forming the CVD film on the metal oxide, so that annealing is done by the NH<sub>3</sub> gas. Dependent claim 22 recites that the dielectric film is a tantalum oxide (Ta<sub>2</sub>O<sub>5</sub>) film. Dependent claim 23 recites that the substrate is heated between approximately 400°C and 700°C. Dependent claim 24 recites that the non-reactive gas is selected from nitrogen, argon, hydrogen gas, or a mixture of these gases. Dependent claim 25 recites that the high melting point metal nitride film is a TiN film. Dependent claim 26 recites that the source gas containing titanium is selected from the group consisting of titanium tetrachloride (TiCl<sub>4</sub>), tetrakis dimethyl amino titanium (TDMAT), tetrakis diethyl amino titanium (TDEAT). Dependent claim 27 recites that the high melting point metal nitride film is a WN film, and WF<sub>6</sub> gas is introduced as a source gas containing tungsten.

Dependent claim 28 recites that the semiconductor device has a capacitive element, a dielectric film, and a CVD high melting point metal nitride film as a protective film between the dielectric film and capacitive element. Dependent claim 29 recites that the semiconductor device has a MOSFET with a gate insulation film and the CVD high melting point metal nitride layer is the lowermost layer of the laminated gate electrode layer formed on the gate insulation film.

The cited art of Nishikawa discloses features that have been discussed in the previous response. Nishikawa discloses a method of forming a dielectric film on a semiconductor substrate in a reduced pressure atmosphere, and then depositing a metal or metal nitride on the dielectric. Nishikawa discloses that hydrogen, carbon and methane released as a normal part of the CVD deposition causes electrical leakage in the dielectric film. Nishikawa discloses that this electrical leakage problem is reduced by using oxygen containing gases in the formation of the conductor film (col. 2, lines 18-27; col. 4, line 66; col. 9, line 15). Nishikawa states that this step is extremely important (col. 2, line 63). The Nishikawa reference discloses that using a reaction gas that contains oxygen at up to 5 sccm (col. 5, line 23) produces an oxygen containing metal film that does not have too high a resistivity to be a useful conductor. The oxidizing gas may be selected from oxygen, peroxide, water, ozone, carbon monoxide, carbon dioxide, nitrous oxide etc (col. 5, line 35 and col. 14, line 47) with the amount kept low through the middle stage of the formation of the conductor (col. 3, line 12) to keep the metal resistance high enough to be a good conductor (col. 4, line 60 and Fig 2).

The cited art of Tamaru discloses a DRAM with a capacitive element that is protected from breakdown under the influence of a TiN film that is CVD deposited on the capacitor dielectric by a passivation film, thus preventing the dielectric from making any

contact with the nitrogen containing reducing gas (col. 3, lines 25 and 49). The Tamaru reference discloses the use of ammonia to passivate the polysilicon lower electrode (col. 2, lines 10-24), but contains no suggestion of any ammonia or reducing gas used after the dielectric is formed (col. 3, lines 30 and 49; col. 4, line 20) until after a oxygen containing titanium source gas has covered the metal oxide (col. 18, lines 33- 40). The Tamaru reference discloses that the metal oxide should not come into contact with reducing gases such as ammonia.

The cited art of Lee discloses a method for making a TiN barrier for a capacitor upper plate to reduce the reactions between the metal oxide and the polysilicon upper electrode (col. 1, line 26). The TiN layer is disclosed as being formed using  $\text{TiCl}_4$ , which may form a material that may attack the metal oxide. This chlorine may be reduced by use of an ammonia anneal which chemically attacks the chlorine and removes it as HCl gas. The anneal step is disclosed as occurring after the TiN deposition.

Applicant respectfully submits that the Nishikawa reference teaches a method that results in an oxidized metal that is not so high in resistivity. Nishikawa does not appear to teach protecting a metal oxide layer that is used as a dielectric in a capacitor. Nishikawa teaches moderately high resistivity conductors versus the dielectric non conductor in the present invention. Nishikawa teaches using an oxidizing ambient to form a slightly oxidized metal layer, in order to prevent the destruction of the film by a reducing ambient. Applicant has amended independent claim 1 herein to make clear that at least one difference between the present invention and the cited reference of Nishikawa is that the present invention utilizes an inert ambient. Specifically, independent claim 1, as amended herein, recites that “...said method comprising a step of treating said

*substrate in an ambient that is non-reactive with respect to said metal oxide formed on said surface of said substrate in said chamber wherein said non-reactive ambient includes at least one of a gas non-reactive with respect to said metal oxide contained in said dielectric film and NH<sub>3</sub> gas ...”, and not the oxidizing ambient of the cited reference of Nishikawa. Applicant submits that if the ambient is intended by the cited reference to oxidize the substrate, then it can not be reasonably said to be non reactive towards the substrate, as required in the claimed invention.*

That the cited reference of Nishikawa teaches using an oxidizing ambient and not an ambient that is non reactive with respect to the underlying metal oxide is clear since the stated goal of the cited reference is to use the oxidizing gas to thereby form the oxygen containing conductor film. Applicant believes that the claim amendments contained herein make it clear that the present invention teaches that the ambient used may be considered to be non reactive with respect to the metal oxide rather than being absolutely inert in all respects.

Applicant respectfully submits that the Tamaru reference teaches and claims using a oxidizing titanium source gas ambient to form a metal layer prior to the introduction of any reducing gas such as ammonia, in order to prevent the disassociation of the metal oxide film by a reducing ambient. Thus the cited reference does not describe or suggest the method of the present application of using a non-reactive ambient, and does not teach the use of ammonia in the ambient. That this is so may be seen since ammonia is a reducing gas that is discussed in the cited reference as being part of the problem the cited reference is directed toward solving.

Applicant respectfully submits that the Lee reference disclose an anneal process that occurs after a small thickness of a TiN barrier layer is formed, and thus does not describe or suggest an anneal of the metal oxide. The cited reference of Lee teaches a method of chemically removing residual chlorine gas in a vacuum system. Applicant respectfully submits that such a reference does not provide motivation for one of skill in the art to combine with the other cited art since it is not directed towards protecting the metal oxide film from reducing ambients as disclosed in the other two cited references.

Applicant respectfully submits that the suggestion on page 3 of the Office Action that it would have been obvious to modify Nishikawa's process with nitrogen to stabilize the tantalum oxide is without basis. This is so because the Nishikawa reference explicitly states that the stabilization of the dielectric film is obtained by using "the copious supply of the oxidizing gas" (col. 2, line 58) to prevent "deficiency of oxygen" (col. 1, line 62) in the dielectric film is "extremely important" (col. 2, line 63), thus clearly not suggesting to one of skill in the art to use a non oxidizing gas such as nitrogen.

Therefore, applicant respectfully submits that independent claim 1, as amended herein, is not obvious over the cited references, for the reasons given above, specifically that the suggested combination of references discloses the use of oxidizing ambients that are reactive to the underlying metal oxide layers.

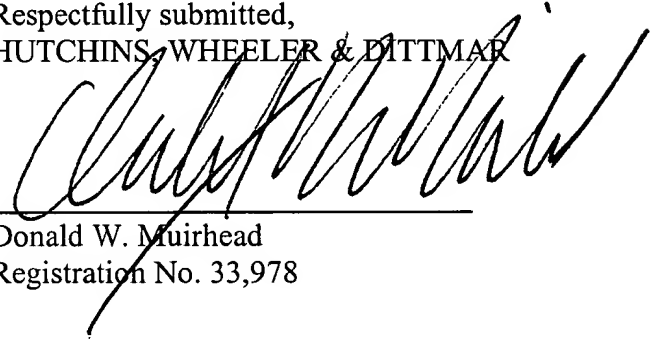
For similar reasons to those given above, independent claim 8 is not obvious over the cited references, specifically that the combination of cited references disclose the use of an oxidizing ambient. Applicant respectfully submits that claims 2-7, 9-11 and 13-29 are therefore also patentable over the cited combination of references at least because they depend either directly or indirectly from independent claims shown above to be patentably distinct and non obvious.



Therefore, for reasons set forth above, applicant respectfully requests that this rejection be reconsidered and withdrawn.

Based on the above, applicant respectfully requests that the Examiner reconsider and withdraw all outstanding rejections and objections. Favorable consideration and allowance are earnestly solicited. Should there be any questions after reviewing this paper, the Examiner is invited to contact the undersigned at 617-951-6676.

Respectfully submitted,  
HUTCHINS, WHEELER & DITTMAR

A handwritten signature in black ink, appearing to read 'Donald W. Muirhead', is written over a horizontal line.

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Clean copy of amendments made herein.

1. A method for forming a semiconductor device having a laminated structure of a dielectric film made from a metal oxide which is formed on a surface of a substrate and a CVD high melting point metal nitride film directly formed thereover, wherein said metal nitride film is directly formed on said dielectric film by introducing a source gas containing said high melting point metal into a chamber in which said substrate is contained,

said method comprising a step of treating said substrate in an ambient that is non-reactive with respect to said metal oxide formed on said surface of said substrate in said chamber wherein said non-reactive ambient includes at least one of a gas non-reactive with respect to said metal oxide contained in said dielectric film and  $\text{NH}_3$  gas,

keeping said temperature of said substrate at a prescribed temperature, before said source gas containing said high melting point metal is introduced into said chamber.

11. The method for manufacturing a semiconductor device according to claim 1, said method further comprising;

a step, performed before said CVD high melting point metal nitride film forming step, of heating a substrate onto which said dielectric film is formed, in said chamber while introducing therein said non-reactive gas; and

a step of forming said high melting point metal nitride film on said dielectric film by introducing a gas mixture comprising said  $\text{NH}_3$  gas and said non-reactive gas, said non-reactive gas in an amount equal to or larger than said  $\text{NH}_3$  gas, and said source gas containing said high melting point metal in an amount less than said  $\text{NH}_3$  gas and said non-reactive gas.